

# Perturbative theory approaches to the metastable phase decay

V Kurasov

## Abstract

The perturbative theory of the nucleation kinetics is analyzed. A new improvement is suggested and compared with numerical calculations.

## 1 Introduction

The global kinetics of the nucleation process was the subject of interest during the last few decades. Various approaches to the description of nucleation kinetics were elaborated in different external conditions [1] - [8] for different systems. One of the most popular is nowadays the perturbation theory approach presented in [4]. It was formulated for the external conditions of the "decay" type: at the initial moment of time the initial supersaturation is created in the system by some external action and later no further external influence can be observed - the system evolution occurs only due to internal processes of the droplets formation and the vapor consumption by the growing droplets. This type of external conditions is rather spread both in the

experimental investigations and in the theoretical descriptions. The reason is evident: on one hand the amplitude value of supersaturation is regulated by an external influence, on the other hand the form of the back side of the droplets size spectrum and characteristic duration of the nucleation period is governed by internal process of droplets formation and growth which gives information about the nucleation origin.

Here we shall analyze the perturbation theory [4] in kinetics of the metastable phase decay. The structure of our analysis will be the following:

- At first we shall see that the recipe given by the perturbation theory leads to the non-uniform decompositions
- Then it will be shown that the perturbation approach in the first approximation (it is rather difficult to speak about the further approximations because even the first approximation can not be calculated analytically up to the very end) can be treated as the monodisperse approximation
- A precise solution of evolution equations will be presented and it will be compared with the perturbation theory approach. It will be shown that the error of the perturbation theory approach will be essential
- A new version of monodisperse approximation has been proposed. This approximation is much more accurate than that given by the perturbation theory

## 2 Reduction of the balance equation

The value of supersaturation  $\zeta$  is defined as the ratio

$$\zeta = \frac{n}{n_\infty} - 1$$

where  $n$  is the number density of molecules in mother phase and  $n_\infty$  is the number density of molecules in the saturated mother phase. Initial value of supersaturation is marked as  $\zeta_0$ .

The balance equation in [4] can be written as

$$\frac{\zeta_0}{\zeta(t)} - 1 = A \int_0^\infty \rho^k g(\rho, t) d\rho$$

for the distribution function  $g(\rho, t)$  which satisfies the continuity equation

$$\frac{\partial g(\rho, t)}{\partial t} = -v(t) \frac{\partial g(\rho, t)}{\partial \rho}$$

with initial condition

$$g(0, t) = \frac{I(\zeta(t))}{v(t)}$$

Here  $\rho$  is the "size" of the embryo which grows with velocity

$$v = \frac{\zeta}{t_0}$$

independent on  $\rho$ ,  $A$ ,  $k$  and  $t_0$  are some parameters. Then the number of molecules in the embryo of the "size"  $\rho$  will be proportional to  $\rho^k$  which explains the sense of the first equation as the balance one.

One can easily reduce this system of equations to

$$\frac{\zeta_0}{\zeta(t)} - 1 = A \int_0^t (t - t')^k \frac{I(\zeta(t'))}{v(t')} dt' \quad (1)$$

with slightly another value of parameter  $A$ .

The case  $k = 0$  is extracted by the possibility of the analytical solution of equation (1) which can be reduced to the first order differential equation

$$\zeta_0 \frac{d}{dt} \zeta(t) = -A \zeta(t)^2 \frac{I(\zeta(t))}{v(t)} \quad (2)$$

with an evident integration. So, we shall discuss this case later as well as the case of small  $k \ll 1$  which can be solved on the base of the solution at  $k = 0$ .

### 3 Singular terms in decompositions

Having extracted the small parameter

$$\epsilon = (\zeta_0 \frac{dH}{d\zeta})^{-1}$$

where  $H$  is the height of activation barrier in units  $k_B T$ , one can easily see that it approximately equals to the inverse number of molecules in a critical cluster. This parameter will be the small parameter of the perturbation theory.

Certainly, after the calculation of all terms in decompositions of the perturbation theory approach and their summation one can get something accurate. The problem is to get concrete results in frames of approximations which can be analytically calculated at least in main features. But already in the first approximation of the perturbation theory there appeared an auxiliary function  $\varphi_k$  given by equation

$$\frac{d\varphi_k}{dx} = \exp(-x^k \varphi_k)$$

$$\varphi_k(0) = 0$$

which does not allow analytical solution. So, already the first approximation (and all other ones) can not be calculated analytically.

From the last remark it follows that it is necessary to have in the first approximation already a good approximation for the real solution. Nevertheless it will be shown here that the first approximation is not accurate enough. Although it was announced in [4] that the decomposition goes on the small parameter similar to the inverse number of molecules in droplet, the first approximation is far from the real solution. This occurs due to the non-uniform character of decompositions. Namely in the balance equation (12) in [4] one can see that  $\rho^k$  transforms into

$$\left(1 - \frac{\epsilon x}{\zeta_0 \tau} + \epsilon w_1 + \dots\right)^k \quad (3)$$

with dimensionless variables

$$x = \frac{\zeta_0 t / t_0 - \rho}{\epsilon}$$

playing the role of shifted size and

$$\tau = \frac{t}{t_0} - \epsilon w_1$$

playing the role of time. All other parameters can be found in [4]. It is evident that the r.h.s. is irregular when  $\tau$  goes to zero. From the first point of view the limit  $\tau \rightarrow 0$  corresponds to the negligible part of formation of droplets. But the careful analysis (see the next section) shows that the nucleation period duration has the relative smallness less than  $\epsilon$  being compared with the imaginary time of consumption of the main part of surplus substance.

## 4 Relative smallness of the nucleation period duration

For all  $k$  we see that

$$-\frac{\zeta_0}{\zeta^2(t)} \frac{d\zeta}{dt} = Ak \int_0^t (t-t')^{k-1} \frac{I(\zeta(t'))}{v(t')} dt' > 0 \quad (4)$$

for  $k > 0$  and

$$-\frac{\zeta_0}{\zeta^2(t)} \frac{d\zeta}{dt} = A \frac{I(\zeta(t))}{v(t)} > 0 \quad (5)$$

for  $k = 0$ . So, we see that the supersaturation is a decreasing function of time.

We exclude the case  $k \ll 1$  from consideration here, since the explicit solution for  $k = 0$  has been presented.

Consider at first the times less than some time  $t_p$  at which the supersaturation  $\zeta$  falls to  $\zeta_0(1 - \epsilon)$ . Then in the leading term equation (1) can be rewritten as

$$1 - \frac{\zeta(t)}{\zeta_0} = (A/v(\zeta_0)) \int_0^t (t-t')^k I(\zeta(t')) dt' \quad (6)$$

For interval  $[\zeta_0(1 - \epsilon), \zeta_0]$  one can evidently use an approximation

$$I(\zeta(t)) = I(\zeta_0) \exp(\epsilon^{-1} \frac{\zeta(t) - \zeta_0}{\zeta_0}) \quad (7)$$

Then

$$1 - \frac{\zeta(t)}{\zeta_0} = (AI(\zeta_0)/v(\zeta_0)) \int_0^t (t-t')^k \exp(-\epsilon^{-1}(1 - \frac{\zeta(t')}{\zeta_0})) dt' \quad (8)$$

or

$$\psi(t) = (\epsilon^{-1} AI(\zeta_0)/v(\zeta_0)) \int_0^t (t-t')^k \exp(-\psi(t')) dt' \quad (9)$$

for the function

$$\psi(t) = \epsilon \left(1 - \frac{\zeta(t)}{\zeta_0}\right)$$

Certainly the last equation can be solved since the renormalization

$$t \rightarrow (\epsilon^{-1} AI(\zeta_0)/v(\zeta_0))^{1/(k+1)} t$$

and

$$t' \rightarrow (\epsilon^{-1} AI(\zeta_0)/v(\zeta_0))^{1/(k+1)} t'$$

brings the last equation to equation with no parameters

$$\psi(t) = \int_0^t (t - t')^k \exp(-\psi(t')) dt' \quad (10)$$

Then the function  $\psi$  is the universal function. Condition  $\psi(t_p) = 1$  makes the time  $t_p$  the universal constant.

For  $t \geq t_p$  solutions of (1) and (10) practically coincides in their functional form. Consider the following equation

$$\frac{\zeta_0}{\zeta(t)} - 1 = A \int_0^{\min(t, t_p)} (t - t')^k \frac{I(\zeta(t'))}{v(t')} dt' \quad (11)$$

which is truncated equation (1). Certainly the solution  $\zeta$  of equation (1) practically coincides with the solution  $\zeta_{tr}$  of equation (11) for  $t \geq t_p$  and is less than  $\zeta_{tr}$  for  $t < t_p$ . So, we get the estimate from above for  $\zeta$ . Since  $I(\zeta_1) > I(\zeta_2)$  for two arbitrary  $\zeta_1 > \zeta_2$ , we see that we know the estimate from above also for the rate of nucleation  $I$ .

One can see that for  $t > t_p$  the solution of (11) is simple, for integer  $k$  the integral transforms into polynomial. Then one can easily show that for all  $k$  except  $k \ll 1$  the solution (11) ensures the rapid decrease of  $\zeta_{tr}$  and  $I(\zeta_{tr})$ . So, we see the rapid decrease of  $I(\zeta(t))$  based on the real solution of (1). Namely, it means that

- The nucleation period - the period of intensive formation of embryos of a new phase is well defined. The lower boundary of this period exists, the long tail of the embryos size spectrum is absent.
- The characteristic relative variation of  $\zeta$  during the nucleation period has the order  $\epsilon$ .
- The characteristic duration of the nucleation period has the order  $t_p$  and in comparison with the time of essential consumption of the metastable phase  $t_{fin}$  it has the smallness  $\epsilon$ .

The last property shows that the singularity in (3) is really important and can not be neglected. It leads to the very approximate results in the first approximation of the perturbation theory.

One can see here another way to calculate the characteristics of nucleation. Really, due to the mentioned properties one can spread equation (10) to the whole interval  $[0, \infty]$  of time, get the universal solution and calculate universal constants

$$q_i = \int_0^\infty t^i \exp(\psi(t)) dt$$

Only  $q_i$  presents all information important for evolution after the nucleation period before the coalescence. For integer  $k$  the number of  $q_i$  is finite, for arbitrary  $k$  one can fulfill decomposition

$$(t - t')^k = t^k \left(1 - \frac{t'}{t}\right)^k = t^k \left(1 - k \frac{t'}{t} + k(k-1) \left(\frac{t'}{t}\right)^2 / 2 - \dots\right)$$

The given number of terms ensures practically ideal result, only first three  $q_i$  are necessary.

This method which is very effective was originally proposed in [5].



## 5 The monodisperse essence of the first approximation

Now we shall analyze the first approximation in order to see the analytical structure. We can consider equation (10) having rewritten it in a form

$$\psi(t) = (k+1) \int_0^t (t-t')^k \exp(-\psi(t')) dt' \quad (12)$$

which is more convenient to get some interesting properties.

The key equation to see the analytical structure is eq. (15) from [4]. One can see that the factor  $\rho^k$  disappears from the subintegral function and this corresponds to the monodisperse approximation of the number of molecules in the droplets. Really, in eq. (15) from [4] only the distribution function  $g$  without  $\rho^k$  is integrated. The formal explanation is simple: since the relative duration of nucleation period is small one can consider that all droplets are formed simultaneously. But this does not work at the nucleation period which is the most important because here all droplets are formed.

Since the monodisperse approximation is adopted it is necessary to get an equation for the number of droplets  $N$  in this approximation. In the mentioned renormalization it looks like

$$\frac{dN}{dx} = \tau^2 \exp\left(-\frac{N}{\tau^{k+1}} x^k\right) \quad (13)$$

where

$$\tau = \left(\frac{1}{k+1}\right)^{1/(k+1)}$$

It is important that all already formed droplets (and even very small ones) have equal contribution in the monodisperse approximation. This leads to an

error. The possible way of correction is to use monodisperse approximation from [9]. It is constructed in the following manner: only droplets formed until some moment of time are included in the monodisperse approximation. It leads to equation of the following type for the rate of nucleation which is proportional to the derivative of  $N$  on  $x$ :

$$I(x) = I(\zeta_0) \exp(-N_{pr}(\frac{x}{l})x^k) \quad (14)$$

$$N_{pr}(x) = \int_0^x I_{pr}(x')dx'$$

Here  $I_{pr}$  is the precise solution of (12). Parameter  $l$  means that only the part (namely  $1/l$ ) of the whole interval produces droplets which are taken into account. The value of  $l$  can be treated as the characteristic halfwidth of the subintegral function  $\rho^k g$ , but later more simple definition will be given.

One can substitute in the last equation the precise solution  $I_{pr}$  by the value calculated on the base of the same monodisperse approximation. Then we come to the self-consistent monodisperse approximation

$$I_{sc}(x) = I(\zeta_0) \exp(-N_{sc}(\frac{x}{l})x^k) \quad (15)$$

$$N_{sc}(x) = \int_0^x I_{sc}(x')dx'$$

It is possible to continue the simplification of the monodisperse approximation. One can see that at the nucleation period the argument of exponent in expression for  $I$  increases very rapidly. So, it is quite possible to assume that for  $x$  at nucleation period the argument  $x/l$  corresponds to practically ideal situation when the action of droplets is negligible even on the rate of nucleation. It can be done when  $l \gg 1$ . Then we come to

$$N(\frac{x}{l}) \approx N_1(\frac{x}{l}) = I(\zeta_0)\frac{x}{l}$$

We see that the functional form of  $I$  here is

$$I(x) = I(\zeta_0) \exp\left(-\frac{x^{k+1}}{l}\right) \quad (16)$$

and it coincides with the functional form in the iteration solution of (12). The iteration procedure is defined in [3] as

$$\psi_{i+1}(t) = (k+1) \int_0^t (t-t')^k \exp(-\psi_i(t')) dt' \quad \psi_0 = 0 \quad (17)$$

and leads to

$$I_1(x) = I(\zeta_0) \exp\left(-\frac{x^{k+1}}{k+1}\right)$$

It is known that this is rather good approximation for the rate of nucleation at least at  $k = 3/2, 2, 3$  typical for nucleation.

The full coincidence will be if we put  $l = k+1$ . This is the most reasonable choice of  $l$ . One can see that here  $l$  attains big values as it has been assumed.

Certainly one can choose  $l$  in a more sophisticated style. The problem is to write and to solve some algebraic equation on  $l$  which can be done in more precise approximations. It is not a real problem and here it is quite sufficient to use the simplest  $l = k+1$ . In any case it can be refined.

Now it is worth to return to the problem of analytical calculation of the mentioned approximations. Now only (16) can be calculated in analytical way. The way to calculate other approximations is the following:

- Consider (16) as the base approximation. Having presented  $I$  as  $I = I_1 \frac{I}{I_1}$  we decompose  $\exp(\ln I - \ln I_1)$  into series of argument  $(\ln I - \ln I_1)$ . It is worth doing because both  $I$  and  $I_1$  have exponential form. Then we come to expression of a type

$$\int_0^x \exp(-x^{k+1}) * Polynomial(x) dx$$

which can be easily reduced to the sum of  $\zeta$ -functions or  $\int_0^x \exp(-x^i) dx$ .

The problem is solved.

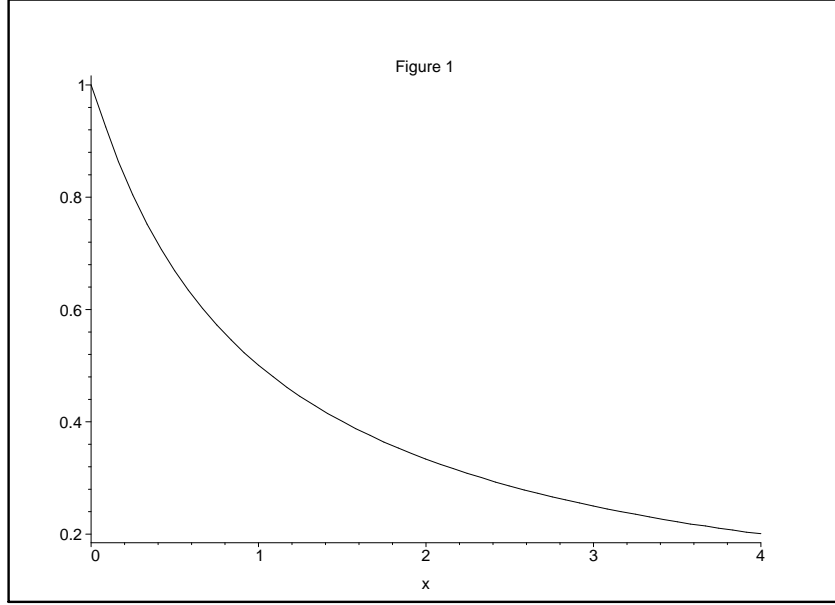
The same method can be applied to calculate further iterations in the iteration procedure (17).

It seems that new approximations will work better than the old ones. Now we shall test all of them.

## 6 Discussion

Here we shall investigate in details all cases which were calculated in [4], namely  $k = 0, 1/2, 1, 2$ . We add here the case  $k = 3$  because it corresponds to formation of embryos under the free-molecular regime in a three-dimensional space which is the most natural case.

The case  $k = 0$  has the analytical solution as the first order differential equation. It is shown in figure 1. One can see that here the rate of nucleation as a function of time (or of coordinate  $x$ ) is shown.



The rate of nucleation as a function of  $x$  forms the droplets size spectrum. One can see that here it is rather long. The tail plays the main role, the number of droplets is infinite at least under the exponential approximation of the nucleation rate.

So, here appears a problem to calculate the total number of droplets. The exponential approximation fails in this question and this opens a problem. Fortunately, this problem has a very simple solution.

One can see that here it is extremely simple to calculate the main characteristic of nucleation - the total number of droplets. Really, the total number of droplets  $N_{tot}$  is simply the amount of surplus substance  $\zeta_0 n_\infty$  divided by

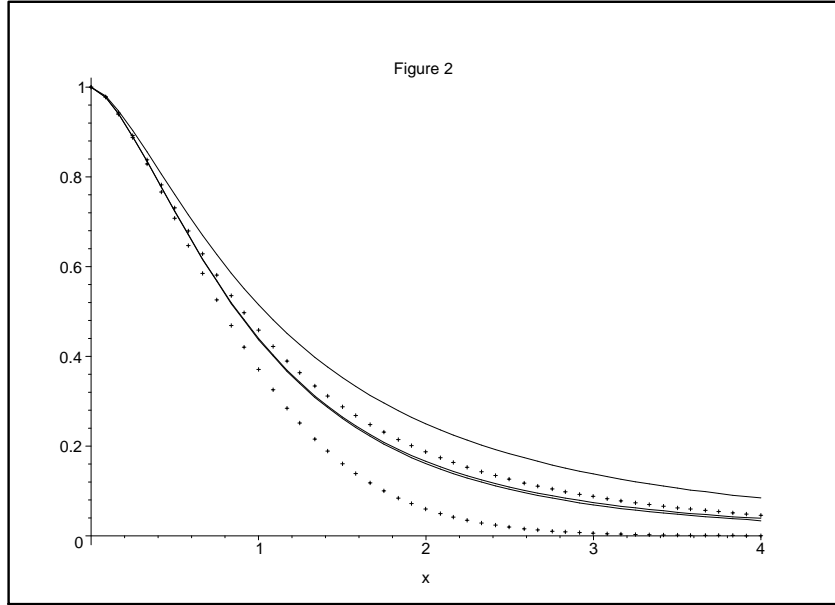
the final number of molecules in the droplet  $\nu_{fin}$ :

$$N_{tot} = \frac{\zeta_0 n_\infty}{\nu_{fin}}$$

Here we see the error of the last model because for  $k = 0$  the rate of growth is zero and the droplets can not become supercritical ones. So, the necessity of external parameter  $\nu_{lim}$  is evident.

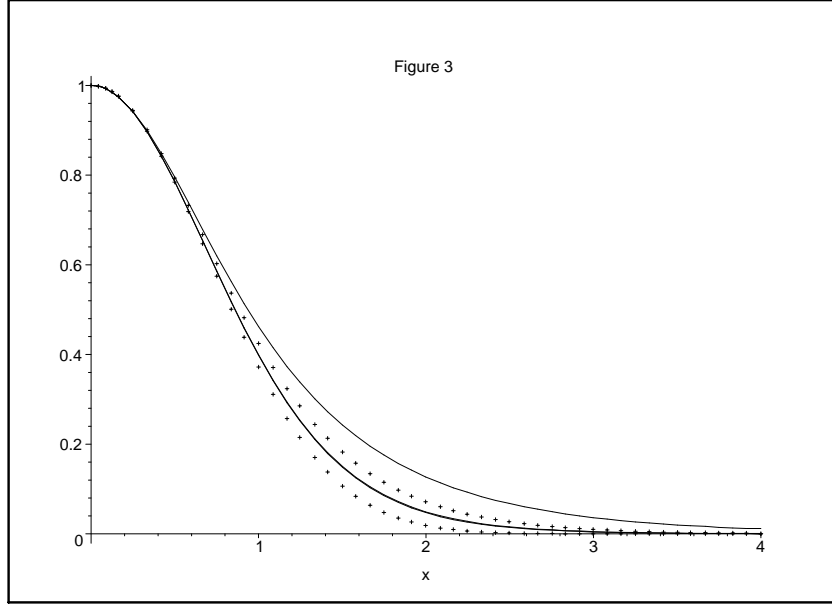
The case of small  $k$  is the most dangerous because on one hand there is no such balance relation as the previous one and on the other hand all droplets play practically equal role in vapor consumption and the number of droplets appeared at the fallen supersaturation is essential.

Consider now the power  $k = 1/2$ . The rates of nucleation in different approximations in this case are drawn in figure 2.



The rate of nucleation is drawn. Here one can see two point curves and two line curves. The upper point curve is the precise solution. Solution with decomposition of kernel can not be separated from the real solution in scale of a picture - the error is negligible. The upper line curve is the approximation of the perturbation theory. It is rather close to the real solution, but still the error exists. The lower line curve is thick - two monodisperse approximations (14) and (15) are drawn here. They can be hardly separated. The approximation of the first iteration (16) is the lower point line. One can see that here the error of the last approximation is essential.

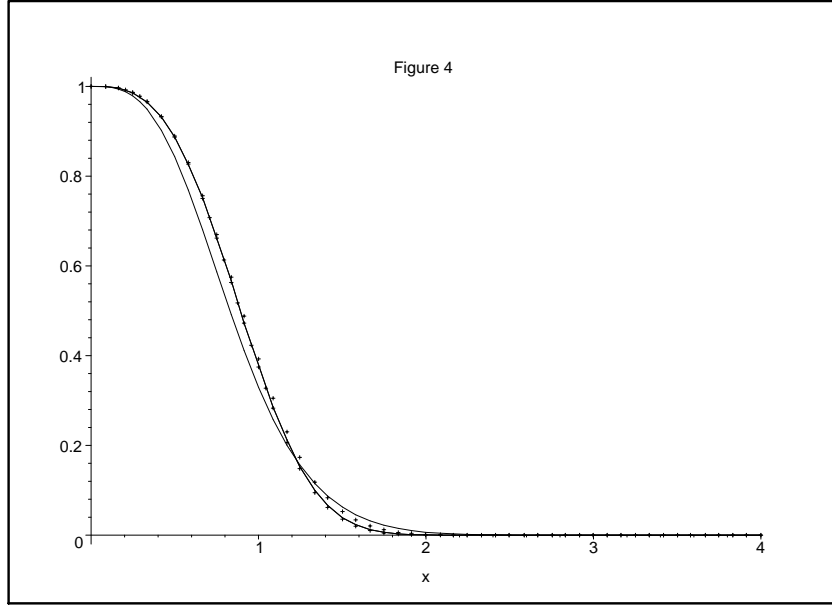
Consider now the case  $k = 1$ . This case can be solved analytically. numerical results are drawn in figure 3.



The rate of nucleation is drawn. Here one can see four curves. The upper

point curve is precise solution. The upper line curve is approximation of the perturbation theory. The lower line curve is thick - there are two monodisperse approximations (14) and (15) which again can not be separated. The lower point curve is approximation of the first iteration. All approximations work well but the perturbation theory approximation has the maximum error. Later this tendency will be stronger.

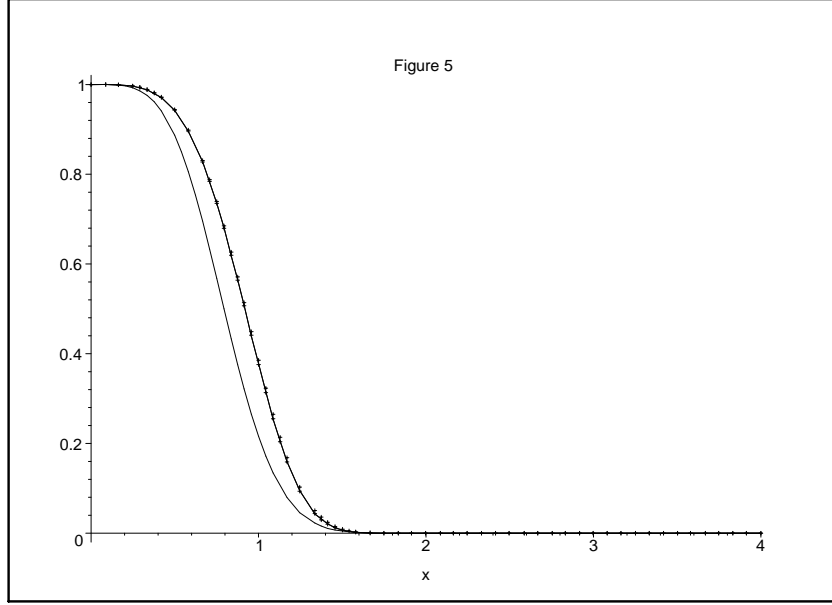
The next case is  $k = 2$ . It is shown in figure 4.



The rate of nucleation is drawn. Only two curves can be seen here. The curves corresponding to the precise solution and approximations (14), (15) and (16) is one thick line with points on it. Another line is the approximation of perturbation theory. Although it has an evident error it seems that with  $k$  becoming great this error will be small. But it is no more than illusion.



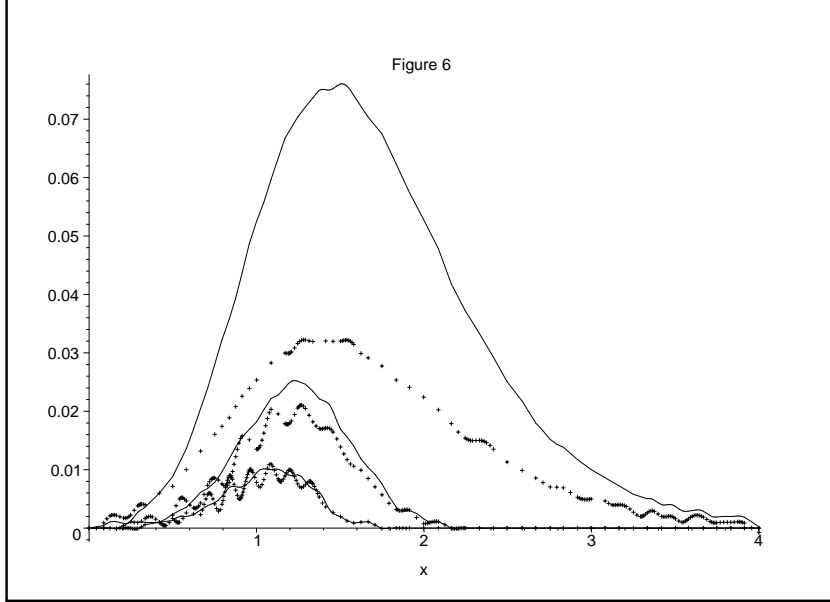
For  $k = 3$  we have the following numerical results which are drawn in figure 5.



The rate of nucleation is drawn. Again one can see two curves here. The curve without points corresponds to the approximation of the perturbation theory. The curve with points corresponds to precise solution and all other approximations. One can see that being compared with the case  $k = 2$  the approximation of perturbation theory goes away from precise solution. This tendency takes place because of a wrong number of essential droplets in the actually monodisperse approximation of the perturbation theory.

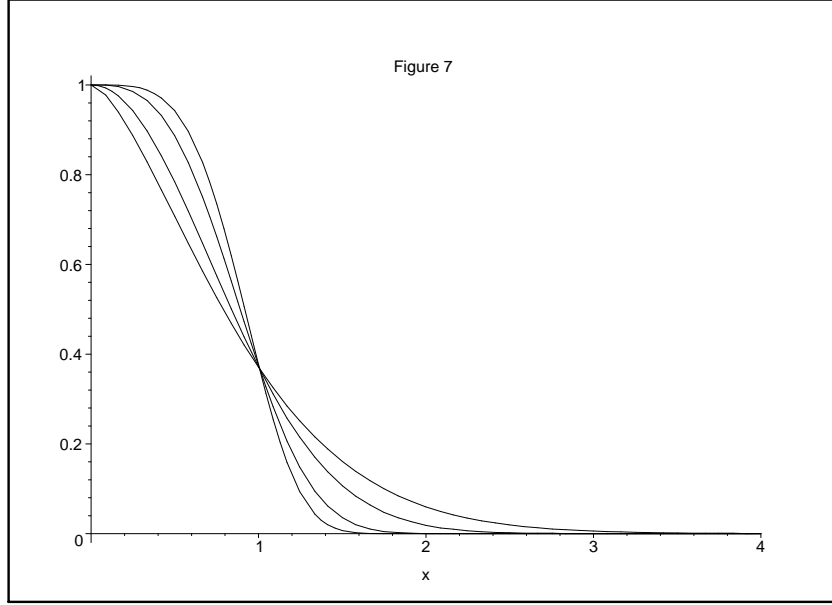
Now one can calculate the errors of new approximations. Since the errors of the perturbation theory can be seen directly in pictures there is no need to discuss it. The errors of approximations for  $k = 1, k = 2, k = 3$  are drawn

in figure 6.



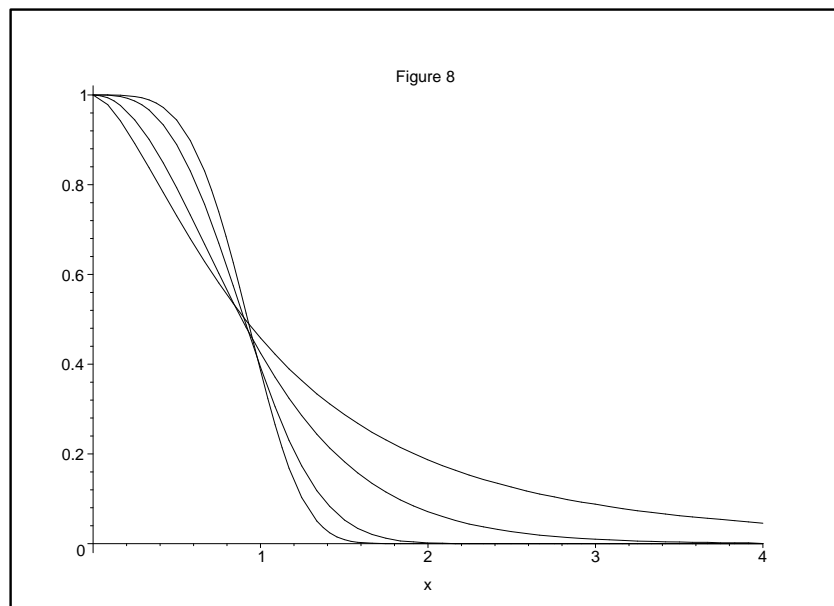
One can see here three pairs of point and line curves. The line curves are approximations (16) for different  $k$ , the point curves are approximations (14), (15) (they practically coincide for all  $k$  with the reasonable accuracy of calculations). The lowest point and line curves coincide (this corresponds to  $k = 3$ ) and it means that for  $k > 3$  there is no advantage of approximations (14) instead of (16). The upper curves correspond to  $k = 1$ , the middle curves - to  $k = 2$ . One can see that for  $k = 1$  the advantage of (14), (15) is essential.

The approximation (16) can lead to some important consequences. Having drawn in figure 7 the approximation (16) for all considered  $k = 1/2, 1, 2, 3$  we see that there is a focus - a point where all curves get together.



This fact can be proven analytically by the simple differentiation. Really, the form of the first iteration is extremely simple  $\sim \exp(x^{(k+1)})$  and at  $x = 1$  the rate of nucleation falls  $e$ -times.

Since the precise solution is not far from the first iteration, one can see the approximate property. It is shown in figure 8 where the precise solutions for  $k = 1/2, 1, 2, 3$  are drawn.



This allows to speak about the property of the precise common length of nucleation under the external conditions of the decay type.

## References

- [1] Tunickii N.N., Journal of physical chemistry vol 15, p. 1061 (1941) (in russian)
- [2] Kuni F.M., Grinin A.P., Kabanov A.S. Kolloidnui journal vol 46, p.440 (1984) (in russian)
- [3] Kuni F.M., Grinin A.P. Kolloidnui journal vol 46, p.460 (1984) (in russian)

- [4] Kukushkin S., Osipov A, J.Chem.Phys. vol. 107 p 3247-3252 (1997)
- [5] Kurasov V.B. Preprint of VINITI 8321-B / 5.12.1986, 40 p.
- [6] Kurasov V., Kinetic theory for condensation in dynamic conditions  
Physical Review E, vol 49, p.3948-3956, 1994
- [7] Kurasov V. Kinetic effects of multi-component nucleation Physica A,  
8612, 2005 58 .
- [8] Kuni F.M. Novojilova T.Yu. Terent'ev I.A., Lett Math Phys. 14 161  
(1987)
- [9] Kurasov V. Decay of metastable multicomponent mixture. arXiv.org get  
cond-mat/9310005